GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 8/13/79

Project Title: Characterization of Metal Aggregates

Project No: G-33-653 Green Card

Project Director: Dr. James L. Gole

Sponsor: National Science Foundation

Agreement Period: From 9/1/79 Until ~~2/28/81~~ 8/31/83 ~~2/28/83~~ (Grant Period)

Type Agreement: Grant No. CHE-7909075, dated 7/27/79

Amount: $44,000 NSF (G-33-653)
3,730 GIT (G-33-347)
$47,730 TOTAL

Reports Required: Annual Progress Report; Final Project Report

Sponsor Contact Person (s):

Technical Matters

William E. Cramer, Program Director
Quantum Chemistry Program
Physical Chemistry & Dynamics Section
Division of Chemistry
Directorate for Mathematical and Physical Sciences, and Engineering
National Science Foundation
Washington, D. C. 20550
202/632-4266

Contractual Matters
(thru OCA)

NSF Grants Official

Ms. Paulette L. Green
MPE/STIA Branch, Section I
Division of Grants and Contracts
Directorate for Administration
National Science Foundation
Washington, D. C. 20550
202/632-5900

Defense Priority Rating: n/a

Assigned to: Chemistry (School/Laboratory)

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date February 2, 1984

Project No. G-33-653 School/~~Lab~~ Chemistry

Includes Subproject No.(s) _____

Project Director(s) Dr. James Gole GTRI / ~~GIT~~

Sponsor National Science Foundation

Title Characterization of Metal Aggregates

Effective Completion Date: 8/31/83 (Performance) 11/30/83 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [X] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [X] Final Report of Inventions
- [X] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Continues Project No. _____ Continued by Project No. _____

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Form OCA 60:1028

Research Progress Report

and

Grant Renewal Request

submitted to the

NATIONAL SCIENCE FOUNDATION

Proposed Amount: $39,000 *Proposed Effective Date:* 9/1/80

Proposed Duration: 12 Months

Characterization of

METAL AGGREGATES

Grant Number: CHE-7909075

Principal Investigator: James L. Gole

Social Security Number: 551-74-2508

Department: Chemistry

Institution: Georgia Institute of Technology
225 North Avenue
Atlanta, Georgia 30332

Endorsements:

Principal Investigator James L. Gole

Department Head Aaron Bertrand

Institutional Administrative Official
Dwight L. Allen

Research efforts during the current grant period can be grouped into six categories.

1) Completion of our first phase of sodium cluster studies. In the hope of obtaining optical spectra for sodium clusters Na_n, we have investigated the supersonic expansion of pure sodium vapor. These studies have led to a much more refined characterization of the cooled clusters produced in this expansion. For a typical expansion at 140 torr backing pressure (oven at 1000°K), we find that 99.75% of the Na_2 aggregates produced are well represented by a vibrational temperature of 50°K and a rotational temperature of 30°K. Approximately 0.25% of the Na_2 molecules are still at temperatures approaching 1000°K. Based on recent matrix isolation studies[1] and the calculations of Martin and Davidson[2] we have attempted to excite fluorescence from Na_3 in the spectral region lying between the $A^1\pi$ and $B^1\Sigma^+$ states of Na_2. Here we focus on the region in which the Franck-Condon factors for the A-X transition drop off sharply and little or no B-X excitation should be observed because of the low temperature characterizing more than 99% of the Na_2 molecules. Unfortunately, the high sensitivity of the laser fluorescence technique coupled with the small component of "hot" Na_2 and the large dimer transition moments leads to severe problems. It may be possible to alleviate some of these problems in the near future through seeding with argon or helium; nevertheless, one of the major problems in characterizing supersonically expanded sodium clusters had been elucidated.

A very intriguing aspect of our sodium studies has been the observation of laser induced atomic fluorescence accompanying the formation of sodium clusters under certain experimental conditions. Upon "single photon" laser pumping at a laser frequency 500 cm^{-1} or more energetic than the sodium D line, we observe atomic fluorescence. Strikingly, this fluorescence is overwhelmingly from the $^2P_{3/2}$ component of the 5890 Å Na ($^2P - {}^2S$) emission. The source of the fluorescence is not a collisional process involving Na_2 and must be associated with the photodissociation of a higher sodium polymer, viz

$$Na_x^* \xrightarrow{h\nu} Na_{x-1} + Na^*$$

As the enclosed figure demonstrates, the atomic fluorescence from $^2P_{3/2}$ varies with laser excitation producing a series of fluctuation bands. More recent mass spectrometric work has demonstrated that the structured atomic fluorescence features for $^2P_{3/2}$ may be correlated with Na_3. It appears that we have observed the photodecomposition of Na_3 via excitation from a shallow "low-lying or ground state" potential to a repulsive excited electronic state. A substantial portion of the spectra shown in Figure 1 have now been run at much higher resolution and no structure can be found in the broad peaks at energies higher than 17650 cm^{-1}. This leads us to correlate the peaks in these figures with discrete lower states and repulsive excited states. We have completed the first phase of the experiments which we intend to do on the sodium system and will soon begin writing up this work. We are also seeking to collaborate with Professor Ernest Davidson in order to obtain further elucidation of our observations.

2) Using a heat pipe oven, we have obtained extensive and previously unanalyzed spectra for Sb_2(B-X). These spectra are obtained under very precise operating conditions primarily because the transition moment for the observed system appears to be quite low and the fluorescence is very sensitive to a variety of experimental effects. Because of this low dimer transition moment and our ability to strongly vary the Sb_2 fluorescence features, we had hoped to obtain spectra for the more prevalent (equilibrium vapor) antimony tetramer under conditions unfavorable for dimer emission. This effort appears to be partially successful. We have obtained what appears to be an Sb_4 spectrum. We are now attempting to substantiate and clarify these observations through nozzle expansion of antimony vapor. We have observed cooling effects; however, the source is not yet perfected so as to observe fluorescence over a wide spectral range. There are still a few problems involving vaporization kinetics; however, it appears that these can be alleviated by running with ultrahigh purity antimony metal.

The spectra for antimony dimer have now been simulated to obtain

vibrational and rotational constants for the B-X system. We have also determined that the spectra are characterized by a thermal distribution at 1200°K.

3) We have now obtained and installed a ring laser to study high resolution aggregate spectra (0.001 cm^{-1} bandwidth at high laser power). The system is currently capable of operation in the Rhodamine dye region (5300-6700 Å); however, in a few weeks we will have the necessary optics for stilbene operation (4200-4800 Å).

4) We have completed initial characterization of the supersonic expansion of pure copper vapor. We have now expanded at temperatures up to 2700°K producing rotational temperatures $\leq$600°K and vibrational temperatures $\leq$700°K. We have begun efforts to seed these expansions with argon and have produced rotational temperatures $\leq$400°K and vibrational temperatures $\leq$450°K. We are currently modifying our system to better accommodate seeded supersonic beams by installing a much more efficient pumping system. Preliminary work using both pure (reprint enclosed) and seeded expansions has indicated the formation and probable observation of laser induced fluorescence from copper trimer. These studies will continue more effectively upon purchase of a new argon ion laser tube so as to obtain sufficient u.v. pumping for stilbene-3 and the coumarin dyes.

5) While waiting to purchase a new u.v. pump laser tube, we have begun a side study to investigate the possibility of a double potential minimum in the ground state of CuO. This project will entail considerable work with the newly obtained ring laser.

6) Calculations on lithium clusters and the Group IB trimers Cu_3, Ag_3, Au_3. This work may be summarized as follows:

Li_3, Li_3^-, Li_3^+:

SCF and SCF-CI calculations have been performed on Li_3, its anion and cation. We predict a value of 1.1 eV for the adiabatic electron

affinity. The Li_3^- bond energy is found to be 0.9 eV versus the 0.4 eV energy required to dissociate Li_3 to dimer and atom. Thus, the bond strength of the anion considerably exceeds that of the neutral parent. The difference in the nature of electron binding to Li_2 and Li_3 can be understood through modification of simple MO concepts. The energy required to dissociate Li_3^+ to $Li_2^+ + Li$ is found to be 1.28 eV. Hence, the bond strength of the cation also greatly exceeds that of the neutral. The Li_3^+ bond energy is comparable to the Li_2^+ dissociation energy (1.24 eV). The adiabatic ionization potential is found to be 3.95 eV. The combination of the present study and those of previous researchers indicates that the Li_3 surface is weakly varying with bond angle and may be characterized by multiple minima. The current results for Li_3 and Li_3^+ are discussed in the light of recent mass spectrometric studies of the trimer.

Cu_3, Ag_3, Au_3:

In order to aid the interpretation of experimental data obtained on small metal clusters, we have carried out calculations to determine the structure and vibrational frequencies which characterize the Group IB clusters Cu_3, Ag_3, and Au_3. These calculations center on the application of the Diatomics in Molecules Approach to the description of clusters containing atoms with one unpaired valence electron in an s orbital. The Group IB trimers are all found to have C_{2v} geometries ($^2B_2$ ground states) with bond angles ranging from 65 to 80°. They should therefore have three Raman active vibrations. The vibrational potentials are found to be very anharmonic and Ag_3 is characterized by two very low frequency modes ($\omega_3 \sim 65\ cm^{-1}$, $\omega_2 \sim 36\ cm^{-1}$). In addition the molecules also appear to be fluxional. The results obtained in this study are compared with recent matrix Raman and visible excitation profiles and a reinterpretation of the matrix Raman data is given.

Principal Investigator

The principal investigator has devoted 30% of his time to the present research efforts outlined in this proposal. This amounts to approximately 25 or more hours per week.

Personnel

Graduate students working on and supported in part by this project include Mr. Gary Green and Mr. Alfred Hanner. Other students participating include Mr. Winfred Crumley. Mr. Randall Childs is also participating in the computational studies. Many of the computations are being done in collaboration with Professor David Dixon, a member of the University of

Minnesota chemistry department. In addition, Dr. Donald Preuss and Dr. S. A. Pace are continuing their collaborations with the group.

Public Relations

Seminars and invited papers describing NSF sponsored work were given at the following locations:

Furman University	11/19/79
Materials Research Society Annual Meeting (Cambridge, Massachusetts)	11/28/79
Air Force Cambridge Research Laboratory	11/26/79
Wesleyan University	11/29/79
Ohio State University	1/17/80
The University of West Florida	2/6/80
The University of Georgia	2/12/80

In addition, papers will be presented at the Houston ACS meeting and the Columbus Spectroscopy Symposium. The PI is also an invited speaker at the 1980 Gordon Conference in High Temperature Chemistry where he will speak in the session on metal clusters.

Publications in Press

"The Electronic Structure of the Lithium Trimer Anion and Cation," with R. A. Eades, D. A. Dixon, and R. Childs.

Publications Submitted

"Theoretical Prediction of the Vibrational Spectra of Group IB Trimers," with J. Richtsmeier and D. A. Dixon.

Publications in Preparation

"The Characterization of Supersonic Sodium Vapor Expansions Including Laser Induced Atomic Fluorescence from Polymeric (Na_n, $n \geq 3$) Sodium," with S. A. Pace and D. R. Preuss.

Statement on Funding

All funds currently provided by the National Science Foundation will definitely be expended at the end of the period for which NSF is currently providing support.

Delineation of Other Research Efforts and Support

The research on metal aggregates which is proposed to the National Science Foundation is not supported in any way by other government agencies. In addition, no proposal involving metal aggregate characterization has been submitted to any agency.

A delineation of other research proposals is as follows:

1) Subcontract to Morgantown Energy Technology Center. Tentative approval to study the kinetics and spectroscopy of high temperature compounds of import in the liquification and gasification of coal. Specifically SiO, SiS, KOH, and NaOH.

Tentative funding level: $67,121
March 1, 1980-March 1, 1981

Budget Justifications

The previously promised allotment for the period September 1, 1980-September 1, 1981 is $35,000.00. We propose that this figure be revised upward 11.43% to meet the rapidly rising cost of expendable supplies and semi-precious metals needed to carry out the proposed research effort. Again, only one graduate student is funded; however, several items and their costs need to be considered. The following are significant changes:

1) The cost of replacing the u.v. pump laser tube necessary to the attainment of laser action from coumarin and stilbene dyes has risen from $8,000 to $10,350 with trade-in since this proposal was written. Because 70+% of our research effort in laser spectroscopy centers on NSF sponsored research, we have allocated $5,500 for a replacement laser tube.

2) The cost of silver used in our aggregate studies has risen by a factor of 4 since this proposal was written. At a conservative estimate, 10 experimental runs will cost in excess of $2,400. This will be the minimum investment which we will have to make taking into account recycling of material.

3) The pumping system currently being used for seeded beam operation while operative is far from optimal. In addition, we have been forced to borrow pumps from other apparatuses in the laboratory for use on the aggregates apparatus. This represents a significant problem for two reasons. Not only are the pumps needed for other experiments but also they have been used with strong oxidants. Their operation is not optimal and they have aged sufficiently (6+ years) so that down time for in-laboratory repair is significant. This problem can be alleviated by installing a 50 CFM Kinney Pump at $3,055.

4) In order to properly run our ring laser, we must purchase a 300 Mhz interferrometer at a cost of $3,190. This was not anticipated in previous budgetary discussions.

5) Optics is an ever present need in the laboratory. The necessary funds to purchase high reflectors, appropriately coated etalons and replacement parts for items damaged in the course of experiment runs on the order of $1,500 to $3,000/year.

6) Our oven systems are not inexpensive to operate. Major costs include heating elements (typically $500-$700), heat shields (typically $380 a set), and crucibles with ore of rather unique design. Therefore, we allocate $2,500/year for this category.

Research efforts during the current grant period can be summarized as follows:

1. Completion of Laser Induced Atomic Flourescence Studies of Bound-Free Transitions in Sodium Trimers. As we have noted in previous technical reports, in the hope of obtaining optical spectra for sodium clusters Na_n, we have investigated the supersonic expansion of pure sudium vapor. A very intriguing aspect of our sodium studies has been the observation of laser-induced atomic fluorescence accompanying the formation of sodium clusters under certain experimental conditions. Previously, we reported the observation of atomic fluorescence,[1] upon "single photon" pumping at a laser frequency 500 cm^{-1} or more energetic than the sodium D-line. Strikingly, the fluorescence was found to be overwhelmingly from the $^2P_{3/2}$ component of the 5890Å $Na(^2P\text{-}^2S)$ emission. We determined that the source of the fluorescence was not a collisional process involving Na_2^* and Na and must be associated with the photodissociation of a higher sodium polymer, viz.

$$Na_x^* \xrightarrow{h\nu} Na_{x-1} + Na^* \qquad x \geq 3$$

The atomic fluorescence from $^2P_{3/2}$ was found to vary with laser excitation producing a series of fluctuation bands (Figure 1). More recent work has demonstrated that the structured atomic fluorescence features for $^2P_{3/2}$ may be correlated with Na_3. The spectra shown in Figure 1 have been studied at a resolution (laser linewidth FWHM) of 0.5 cm^{-1}. Further studies at much higher resolution revealed that no structure could be found in the broad peaks at energies higher than 17650 cm^{-1}. This lead

us to correlate the peaks in this figure with a discrete lower state and repulsive excited states. In other words it appeared that we had observed the photodecomposition of Na_3 via excitation from a shallow "low-lying or ground state" potential to a repulsive excited electronic state. In the last year there have been several extensions of this work. These extensions have demonstrated that the fluctuation bands in Figure 1 are actually hot bands corresponding to a low-lying $^1\Sigma_u^+$ state of Na_3. They are obtained upon a purposeful poisoning of the sodium supersonic expansion which leads to a maximum internal excitation (heating) of 2600 cm^{-1} in both Na_3 and Na_2. The Na_3 dissociation energy is $\sim 3000\ cm^{-1}$ and therefore it is not surprising that photodissociation effects are observed $\sim 500\ cm^{-1}$ to the blue of the Na-D line.

Upon careful modification of the sodium expansions so as to produce a "clean" supersonic beam, the fluctuation bands shown in Figure 1 are no longer present, indicating that they do correspond to hot bands. This being the case, we attempted to excite laser induced atomic fluorescence from cooled sodium trimers by tuning our lasers further to the blue. This effort was quite successful and we obtained the spectra depicted in Figure 2. Here we indicate the fluorescence observed upon monitoring the $^2P_{3/2}$ component of the Na-D-line. Similar spectra are obtained, although with a differing intensity distribution, when the $^2P_{1/2}$ component of the D-line is monitored. Scans to 23000 cm^{-1} reveal no further fluorescence features. Further, more resolved spectra have now been obtained and the first phase

of this project now nears completion. We believe the spectra in Figure 2 correspond to the photodissociation of the ground $^2B_1$ and very low-lying $^2A_1$ Jahn-Teller states obtained upon distortion of a triangular sodium trimer, the $^2B_1$ state corresponding to an obtuse angled configuration and the $^2A_1$ state to an acute angled configuration.

There is an outstanding correlation between the current studies and the two-photon photoionization work of Schumacher and coworkers,[2] as well as the detailed quantum mechanical calculations of Martin and Davidson.[3] It now appears that the phenomena observed here can be extended to the study of other bound-free transitions, furnishing a means of mapping the repulsive states which characterize small metal clusters. This may have great importance for the characterization of photocatalytic processes. Further it appears that one can take advantage of the shallow nature of the bonding potentials characterizing many metal clusters and supersonic expansions in general to obtain "hot band" structure close to the dissociation limit of the ground state of the cluster. Indeed, we are now initiating experiments which involve the gradual poisoning of the supersonic expansion so as to build up "hot band" structure in a "controlled" manner.

There are two further points of interest in Figure 2. From the short wavelength (high frequency) limit of the laser fluorescence spectrum, we obtain a upper bound to the Na_3 dissociation energy. This value, 4300 cm^{-1}, is in good agreement with the work of Martin and Davidson.[3] In Figure 2(a), one

notes several sharp features superimposed on the broad structure which results from direct photodissociation of the trimer. These sharp features correlate precisely with strong Na_2 B-X absorption (note the excitation spectrum above Fig. 2(a)). It was first thought that these features corresponded to Na_2^* emission coincidental with the NaD-line. Further experiments, however have demonstrated that this is not the case. The sharp features correspond to atomic fluorescence via the processes

$$Na_2^* + Na_3 \longrightarrow Na_3^* + Na_2$$

$$Na_3^* \longrightarrow Na^* + Na_2$$

$$Na^* \longrightarrow Na + h\nu$$

The cross section for this energy transfer is some four orders of magnitude larger than that for $Na_2^* \longrightarrow Na$ collisional excitation.

2. Further Confirmation of the Na_3 Dissociation Energy. In order to confirm the upper bound for the Na_3 dissociation energy obtained in the studies outlined above, we have undertaken an experiment involving sodium trimer oxidation. The experiment involves the study of the reaction

$$Na_3 + Cl \longrightarrow NaCl + Na_2^*$$

If sodium trimers react with chlorine atoms, the process to produce the chloride and dimers of sodium is sufficiently exothenic so as to lead to the production of excited states of the dimer. There is reason to believe that the Na_3-Cl reaction will proceed through a relatively long-lived complex and that a reasonable component of the reaction exothermicity will be transferred to the dimer. The short wavelength limit of the observed Na_2 fluorescence then provides an estimate of the Na_2-Na dissociation energy. Initial experiments have been carried out and weak Na_2

fluorescence has now been observed. The short wavelength limit of this fluorescence is consistent with a bond energy in excess of 2300 cm^{-1}. Further improvements are now being made on the system.

3. Studies of Antimony and Bismuth Dimers and Tetramers. We have continued our studies of the antimony system attempting to observe more closely spectra which appear to result from Sb_4 excitation. In addition we have carried out some studies with bismuth supersonic expansions primarily as a result of the recent matrix isolation studies of Bondebey and coworkers.[4] We have observed relatively extensive Bi_2 spectra and weak fluorescence which appears to correlate with the Bi_4 systems observed by Bondebey in the matrix. In addition, we find that the bismuth expansions are much more easily controlled than those for antimony. In contrast to the relatively straight forward excitation of Bi_4, Bondebey, et.al., have been unable to observe fluorescence from Sb_4. This is consistent with the weak Sb_4 and Sb_2 spectra characterizing our own experiments. Bondebey and coworkers have observed laser Raman spectra for Sb_4 and the constants which these workers have obtained for the ground state will soon be available to us for further interpretation of our Sb_4 fluorescence spectrum. We anticipate continuing both our supersonic expansion and heat pipe studies of antimony and bismuth correlated closely with the results obtained by Bondebey and coworkers.

4. Preliminary Efforts to Study CuO. In our previous technical report, we noted a side study to investigate the possibility of a double potential minimum in the ground state of CuO. Unfortunately, we have been unable to produce a cooled CuO beam with a wide variety of possible starting materials. In all cases we have obtained a reduction to copper and observed fluorescence from a supersonically expanded copper beam. We anticipate further efforts on this project once a good "seeded" supersonic expansion can be obtained.

5. Supersonic Seeded Copper and Silver Expansion. We have completed the installation of a much more efficient pumping system to better accomodate seeded (helium or argon) supersonic expansions. We will continue to probe newly observed band systems which we have tentatively attributed to copper trimer. An important aspect of this effort has been the purchase of a 50 CFM roughing pump. This device has also greatly aided our sodium studies. We have now also obtained a new, more versatile chamber which we are currently modifying for use in our aggregate studies.

We have carried out one preliminary experiments on silver, however, these studies will be temporarily halted while careful system parameterization is achieved with copper. Our preliminary results indicate that the appropriate technology developed for copper expansion will be readily extendible to silver.

Further aides to this aspect of our projects have been the acquisition of a new argon ion laser tube so as to obtain sufficient u.v. pumping for the coumarin dyes and stilbene. In addition, we have now obtained the necessary materials to

extend our ring laser system to the coumarin and stilbene regions.

6. Quantum Calculations on Metal Clusters. We have now published two papers on lithium trimer anion and cation clusters and the trimers of the Group IB metals; Cu_3, Ag_3, and Au_3. Copies of these papers are included. We are completing extensive calculations on the clusters of the alkali and Group IB metals and we anticipate that two papers will soon be submitted, entitled:

a) "An Exploration of the Structure of Alakli Clusters Using the Diatomics-in-Molecules Method"

b) "The Characterization of the Structure and Vibrational Spectra of the Group IB Clusters Using the Diatomics-in-Molecules Method"

7. Bond Energies for Alkali Metal Hydroxides. We have taken advantage of the technology used to study alkali (sodium) clusters to obtain "direct" measurements of alkali hydroxide (M-OH) bond strengths. The alkali hydroxides represent extremely important species in energy generating systems yet their is little direct information on the bond strengths of these species. Bond energies have been determed using indirect flame techniques (metal atom depletion studies) and in some cases mass spectrometry. Mass spectrometric results are troubled since the alkali hydroxides tend to vaporize as dimers. Our direct measurements of these bond strengths have been accomplished using chemluminescent techniques. They indicate strengths for NaOH and KOH significantly higher than those given in the literature.

Principal Investigator

The Principal Investigator has devoted 30% of his time to the present research efforts outlined in this proposal. This amounts to approximately 25 or more hours per week.

Personnel

Graduate students working on and supported in part by this project include Mr. Gary Green and Mr. Winfred Crumley. Other students participating include Ms. Beatriz Cardelino and Mr. Alfred Hammer. Mr. Randall Childs is also participating in the Computational Studies. Many of the computations are being done in collaboration with Professor David Dixon, a member of the University of Minnesota's Chemistry Department. In addition, Dr. Donald Preuss and Dr. S.A. Pace are continuing their collarobations with the group.

Public Relations

Seminars and invited papers describing NSF sponsored work were given at the following locations:

1.	179th A.C.S. National Meeting	3/26/80
2.	Armstrong State College	4/14/80
3.	Southeastern Theoretical Chemistry Conference	5/09/80
4.	Columbus Spectroscopy Symposium	6/15/80
5.	Gordon Conference on Atomic and Molecular Interactions	7/21/80
6.	Gordon Conference on High Temperature Chemistry	8/08/80
7.	Aerodyne Research Incorporated	8/12/80
8.	180th National A.C.S. Meeting (Las Vegas)	8/27/80

9.	The University of Minnesota	10/27/80
10.	The University of Iowa	10/29-30/80
11.	North Dakota State University	10/31/80
12.	Clemson University	11/13/80
13.	Furman University	11/14/80
14.	Electrooptics Laser 80 Symposium	11/19/80
15.	State University of New York at Binghampton	11/21/80

In addition, invited papers and seminars will be given at the 181st. A.C. S. Meeting, the Columbus Spectroscopy Symposium and the University of Pittsburgh, Brown University, Drexel University and Bell Laboratories.

Publications

"The Electronic Structure of the Lithium Trimer Anion and Cation", with R.A. Eades, D.A. Dixon and R. Childs, J. Chem. Phys., 72, 6368 (1980).

"Theoretical Prediction of the Vibrational Spectra of Group IA Trimers", with S. Richtsmeier and D.A. Dixon, Prec. Natl. Acad. Sci., 77, 5611 (1980).

Publications in Preparation

"Evidence for Photodissociation of Polymeric Sodium Obtained in Supersonic Expansion - Observation of Trimer Fluctuation Bands", with G.J. Green, S.A. Pace and D.R. Rreuss.

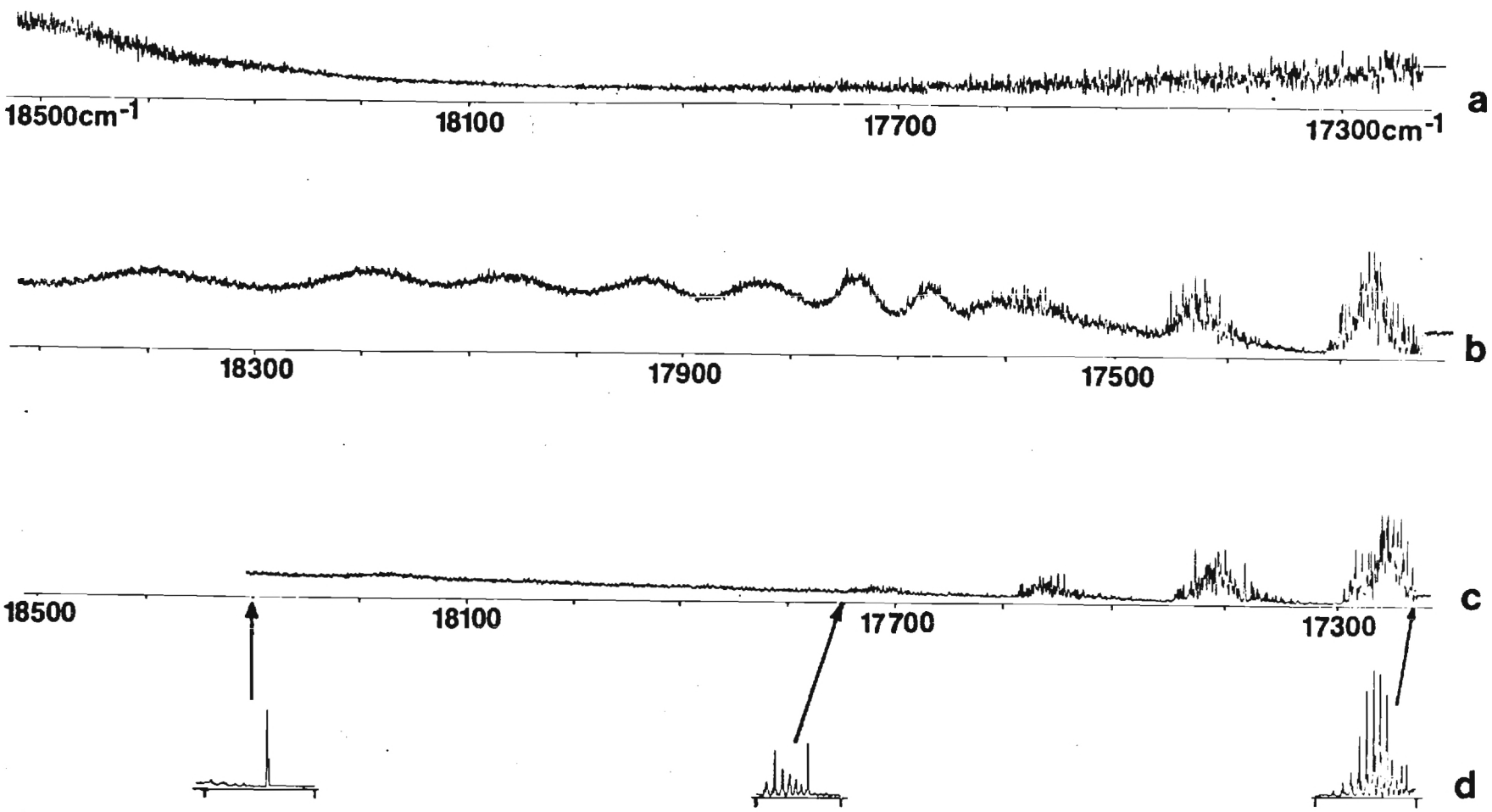
Anticipated Publications (near term)

"Laser Induced Excitation Spectra for Sb_2 $B\,^1\Sigma_u^+$-$X\,^1\Sigma g^+$, and Sb_4" with G.J. Green and S.A. Pace.

"The Dissociation Energies D(M-OH) of the Alkali Hydroxides", with B. Cardelino and W. Crumley.

Figure Caption

Spectra, as a function of dye laser excitation frequency, of supersonically expanded sodium including (a) an excitation spectrum showing the onset of Na_2 $B^1\Sigma_u^+ - X^1\Sigma_g^+$ (~18000 cm^{-1}) fluorescence and the tail of Na_2 $A^1\Pi_u - X^1\Sigma_g^+$ total fluorescence, (b) laser induced atomic fluorescence from $^2P_{3/2}$ Na^* including fluctuation bands at ν(laser) > 17500 cm^{-1}, (c) minimal laser induced atomic fluorescence from $^2P_{1/2}$ Na^* and (d) fast photoluminescence scans indicating relative magnitudes of Na D-line and Na_2 A-X resonance fluorescence (tick marks indicate ν = 16000 and 18000 cm^{-1}). The lower frequency features appearing in scans (b) and (c) (ν_{laser} < 17600 cm^{-1}) correspond to Na_2 fluorescence coincidental with the D-line components.


18500cm-1
18100
17700
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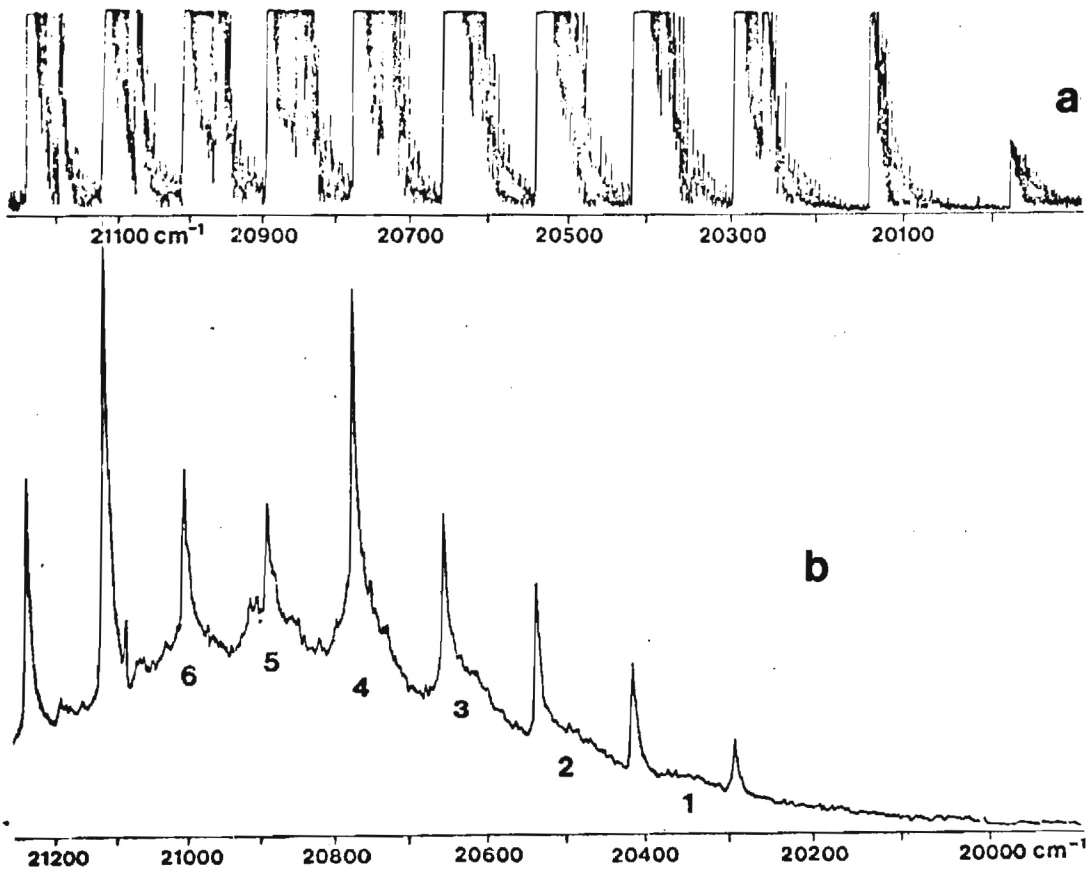
17500
b
18500
18100
17700
17300
c
d

Figure 1

Figure 2

Spectra, as a function of dye-laser excitation frequency, of supersonically expanded sodium including (a) an excitation spectrum showing Na_2 $B^1\Sigma_u^+$-$X^1\Sigma_g^+$ fluorescence, (b) laser induced atomic fluorescence at high expansion pressures and (c) at somewhat lower expansion pressures for the $^2P_{3/2}$ component of the Na-D line.


a
21100 cm⁻¹
20900
20700
20500
20300
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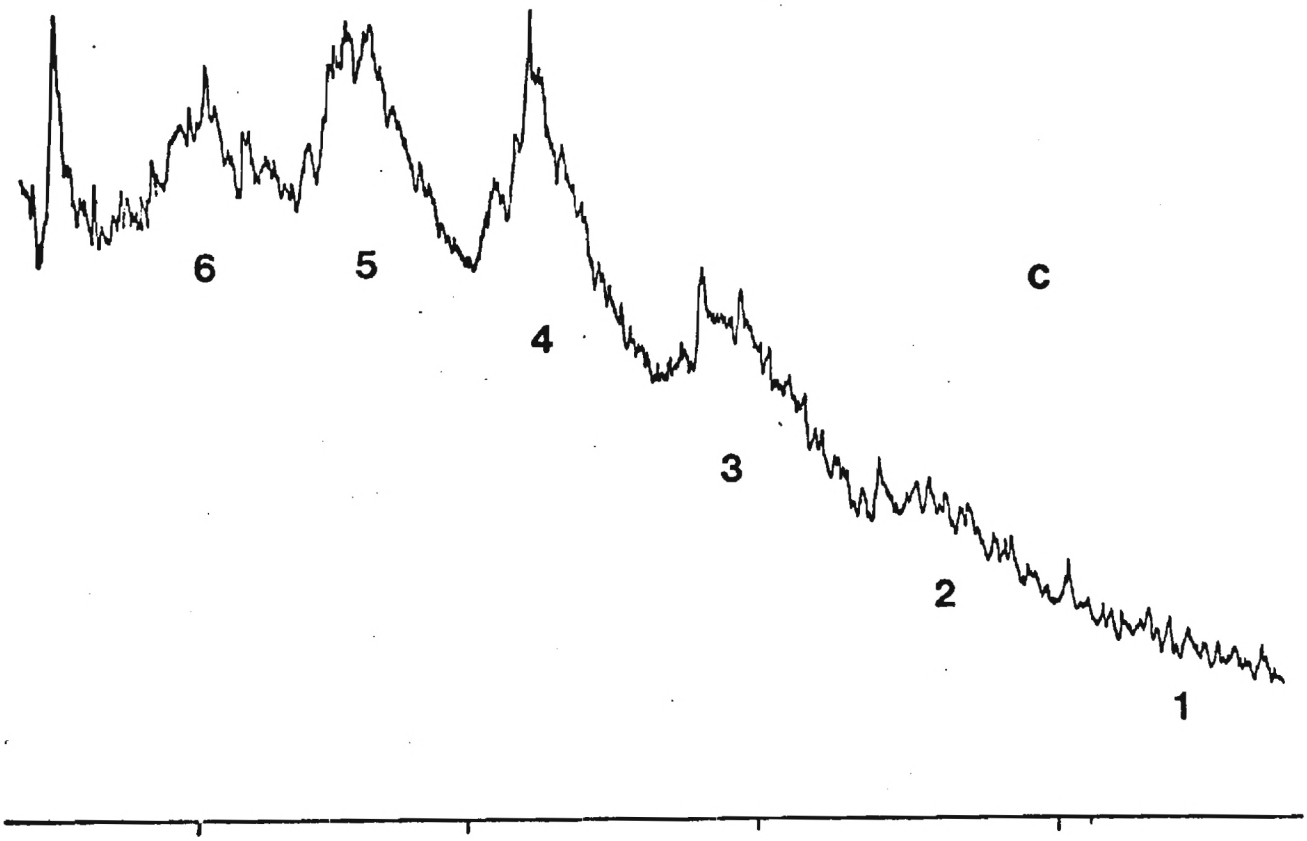
b
6
5
4
3
2
1
21200
21000
20800
20600
20400
20200
20000 cm⁻¹


6
5
4
3
2
1
c

APPENDIX VI

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I–PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Tech Research Institute Admin. Bldg.,Georgia Inst. of Tech. Atlanta, Georgia 30332	Quantum Chemistry	CHE-7909075
	4. Award Period From 9/1/79 To 8/30/83	5. Cumulative Award Amount $122,000

6. Project Title

Characterization of Metal Aggregates

PART II–SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

The characterization of metal clusters and their oxidation contributes insight on a sparsely explored middle ground bordered on the one side by the study of bonding and reactivity involving atoms, diatomic molecules, and other small monomeric gas phase species and on the other by the solid state physicist, surface chemist, and metallurgist. As a contribution to the understanding of this intermediate region, our research effort has employed a unique combination of experiment and theory in order to model the molecular structure and bonding in small metal aggregates (M_n, $2 \leq n \leq 6$) and their ions and to characterize the detailed interactions associated with the oxidation of these species. The experimental research effort has entailed the development of appropriate material science in the formulation of sophisticated techniques and sources for the sampling of high temperature-high pressure systems. Developed sources have been used to produce small metal clusters whose interactions with light and therefore optical signatures have been probed using modern laser excitation techniques in order to evaluate cluster molecular electronic structure and bonding. In close coupling with the optical studies has been the mass spectrometric sampling of the aggregate source constituents. Initial characterization of aggregate metathesis has involved the study of light emission (chemiluminescence) from highly exothermic aggregate oxidation. The research effort has focused primarily on the alkali and coinage metals although some effort has also involved the elements nickel and antimony. There is reason to believe that the basic properties (geometry, bond strength, reactivity) of small metal clusters play an important role in our understanding of the fundamental mechanisms of catalysis and numerous chemical conversions, the study of cluster oxidation providing information which will be useful for the assessment of short (localized) and long range factors affecting surface oxidation. Therefore these studies may well provide information which contributes to the formulation of general criteria for improving materials conversion processes, the development and improvement of energy conserving devices, and the identification of factors which may be modified to lessen material degradation.

PART III–TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (√)	Approx. Date
a. Abstracts of Theses		X			
b. Publication Citations		X			
c. Data on Scientific Collaborators		X			
d. Information on Inventions		--			
e. Technical Description of Project and Results		X			
f. Other *(specify)*					

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
James L. Gole	James L. Gole	1/16/84

NSF Form 98A (5-78) Supersedes All Previous Editions

Form Approved OMB No. 99R0013

Part III

a. CHEMILUMINESCENCE STUDIES OF HIGHLY EXOTHERMIC REACTIONS AND LASER INDUCED FLUORESCENCE STUDIES OF SMALL METAL CLUSTERS FORMED IN SUPERSONIC EXPANSION

A THESIS
Presented to
The Faculty of the Division of Graduate Studies
by
Gary James Green

In Partial Fulfillment of the
Requirements for the Degree
Doctor of Philosophy
in the School of Chemistry
Georgia Institute of Technology
June, 1982

SUMMARY

The chemiluminescent emission from silicon and germanium monosulfide resulting from the reaction of silicon and germanium metal with carbonyl sulfide has been studied under both single and multiple collision conditions. Included in this study is the observation of the SiS and GeS $a^3\Sigma^+ - X^1\Sigma^+$ and Sis $b^3\Pi - X^1\Sigma^+$ intercombination band systems. The temperature dependence of the observed single collision spectra is analyzed to deduce the nature of the metal reactant beams and to determine the activation energies for formation of SiS* ($a^3\Sigma^+$, $b^3\Pi$) and Ges* ($a^3\Sigma^+$). The significance of the activation energies is discussed. Lower bounds of 144.1±1.6 kcal/mole and 132.2±1.0 kcal/mole are determined for D_0^o(SiS) and D_0^o(GeS), respectively. The nature of the single collision SiS $a^3\Sigma^+ - X^1\Sigma^+$ emission system is examined by determining the vibrational population distribution in the $a^3\Sigma^+$ state resulting from the Si + OCS reaction. Multiple collision spectral studies are used to initiate the exploration of collisional quenching.

An intense source has been developed to study the reactions of boron atoms with O_2, NO_2, N_2O, ClO_2, and O_3. The chemiluminescent emissions which characterize the bimolecular reaction of boron with O_2, N_2O, ClO_2, and O_3 are dominated by the $A^2\Pi - X^2\Sigma^+$ band system of BO. In contrast, the chemiluminescence from the bimolecular boron-NO_2 reaction is dominated by strong BO_2 $A^2\Pi_u - X^2\Sigma_g$ emission. A reaction mechanism consistent with these observations is proposed.

A supersonic expansion of pure sodium vapor has been used to form small sodium clusters M_n, $n > 2$. Discussion focuses on the characterization of such an expansion carried out for a wide range of experimental conditions and the analysis of laser induced atomic fluorescence (LIAF) resulting from the photo-

dissociation of triatomic sodium clusters. Considered are: 1) the nature of observed "fluctuation" bands corresponding to the pumping of bound-free transitions in Na_3 which yield ^2P Na atoms (Na D-line emission) and ground state $^1\Sigma_g^+$ Na_2 and the different spectral characteristics associated with these transitions as they are observed in high purity, mildly disrupted, or highly disrupted supersonic expansion; 2) the possibility of controlled "hot band" formation through disruption of the expansion, allowing the mapping of vibronic structure in the ground electronic and low-lying electronic states of the weakly bound sodium trimer molecule; 3) the determination of an upper bound $D_o < 4250\ cm^{-1}$ for the Na-Na_2 bond energy from an analysis of the sodium trimer LIAF spectrum; and 4) the observation of very efficient energy transfer between sodium dimer and polyatomic sodium.

A continuous, high-temperature seeded supersonic molecular beam source has been developed and demonstrated with antimony metal as the sample. The supersonic expansion of an antimony vapor/argon carrier gas mixture is used to obtain "cooled" antimony dimer optical spectra via laser induced fluorescence corresponding to the Sb_2 $BO_u^+ - X^1\Sigma_g^+$ band system. The Sb_2 spectrum obtained in the seeded supersonic expansion is contrasted to that obtained for Sb_2 existing in an equilibrium vapor of antimony at the same temperature at which the seeded beam source was operated.

b.

1. "The Electronic Structure of the Lithium Trimer Anion and Cation", J. L. Gole, R. A. Eades, D. A. Dixon and R. Childs, J. Chem. Phys. 72, 6368 (1980).

2. "Theoretical Prediction of the Vibrational Spectra of Group IB Trimers", S. Richtsmeier, J. L. Gole, and D. A. Dixon, Proceedings of Nat. Acad. Sci. 77, 5611 (1980), 78, 7259 (1981).

3. "The Electronic Structure of Small Group IA and Group IB Metal Clusters", with S. C. Richtsmeier, R. A. Eades, and D. A. Dixon, A.C.S. Symposium Series No. 179 - Metal Bonding and Interactions in High Temperature Systems with Emphasis on Alkali Metals (Ed. J. L. Gole and W. C. Stwalley) Am. Chem. Soc., Wash. D. C. (1982), pg. 177.
4. "The Characterization of Supersonic Sodium Vapor Expansions Including Laser Induced Atomic Fluorescence from Trimeric Sodium", with S. A. Pace, D. R. Preuss and G. J. Green, J. Chem. Phys. 76, 2247 (1982).
5. "Bound-Free Transitions in Weakly Bound Metal Aggregates", with Gary Green, A.C.S. Symposium Series No. 179 - Metal Bonding and Interactions in High Temperature Systems with Emphasis on Alkali Metals (Ed. J. L. Gole and W. C. Stwalley) Am. Chem. Soc., Wash. D.C. (1982), pg. 125.
6. "Laser Spectroscopy of Refractory Compounds", presented as an invited contributation to Electro-Optics Laser 80, Proceedings of the Electro-Optics/ Laser 80 Conference and Exhibition, pp. 127-140.
7. "Metal Cluster Oxidation: Chemiluminescence from the Reaction of Sodium Polymers (Na_n, $n > 3$) with Halogen Atoms (X=Cl,Br,I)", with W. H. Crumley and D. A. Dixon, J. Chem. Phys. 76, 6439 (1982).
8. "The Electronic Structure of Alkali Trimer Anions and Cations", with R. A. Eades, M. L. Hendewerk, R. Frey, and D. A. Dixon, J. Chem. Phys.. 76, 3075 (1982).
9. "The Structure of Mixed Alkali Metal Trimers", with S. C. Richtsmeier, M. L. Hendewerk, and D. A. Dixon, J. Phys. Chem. 86, 3932 (1982).
10. "The Structure of Group IB Metal Clusters, M_n, n = 4-6", with S. C. Richtsmeier and D. A. Dixon, J. Phys. Chem. 86, 3937 (1982).
11. "The Structure of Group IA Metal Clusters, M_n, n = 4-6", with S. C. Richtsmeier and D. A. Dixon, J. Phys. Chem. 86, 3942 (1982).

12. "Laser Induced Photodissociation of Trimeric Sodium" in Proceedings of the International Conference on Lasers '81 (New Orleans, Louisiana), pg. 244.
13. "Photodissociation and Oxidation of Small Metal Clusters", Bull. Am. Phys. Society 27, 304 (1982).
14. "Laser Spectroscopy of Cooled Metal Clusters: Copper Dimer", with V. Bondybey and J. H. English, J. Phys. Chem. 86, 2560 (1982).
15. "Electron Affinities of the Alkali Dimers Na_2, K_2, and Rb_2", with H. Partridge, D. A. Dixon, S. P. Walch, and C. W. Bauschlicher, J. Chem. Phys. 79, 1859 (1983).
16. "Laser Induced Excitation Spectroscopy of Copper Trimer Obtained in Supersonic Expansion", with W. H. Crumley, to be submitted to Jour. Phys. Chem. Communications.
17. Book: Metal Bonding and Interactions in High Temperature Systems with Emphasis on the Alkali Metals, A.C.S. Symposium Series No. 179 co-edited with W. C. Stwalley, Am. Chem. Soc., Wash. D. C. (1982).

c.

Collaborators

1. Donald R. Preuss - graduate student - Ph.D. 1979
2. Gary J. Green - graduate student - Ph.D. 1982
3. W. H. Crumley - graduate student
4. S. A. Pace - postdoctoral research associate
5. R. H. Childs - Computer Center, Georgia Institute of Technology

Through collaborative efforts with the University of Minnesota

6. David A. Dixon - Assistant Professor, Department of Chemistry
   Currently E. I. Dupont Nemoirs and Co.
7. S. C. Richtsmeier -graduate student
8. R. A. Eades - graduate student

9. M. L. Hendewerk - undergraduate researcher

10. R. Frey - undergraduate researcher

Through collaborative efforts with Bell Laboratories

11. Vladamir Bondebey - Ph.D. (staff)

12. J. H. English - Technician (staff)

e. Technical Progress Report

Because of their probable importance to the understanding of the fundamental mechanisms of catalysis and numerous chemical conversions, the basic properties (geometry, bond strength, reactivity) of small metallic clusters, M_n ($2 \leq n \leq 6$) have become the subject of intense theoretical and experimental study. In addition, their characterization contributes to our understanding of the nucleation and growth of small metal particles and the development of features inherent in the bulk metallic phase.

The surface physicist and metallurgist have greatly enlightened our understanding of the macromolecular features and hence the electronic structure of bulk metals. The molecular physicist and physical chemist have provided a wealth of information on metal atoms, diatomic molecules, and other small monomeric species. These efforts have been impressive, yet they leave open a middle ground whose exploration is still in its infancy. Although it is an intuitive assumption that the electronic properties of small metallic particles lie intermediate between atomic properties and bulk metal characteristics, this picture has been at best only semiquantitative. As a contribution to the understanding of this intermediate region, the emphasis of our research effort has been the attainment of basic information, both experimental and theoretical, about the molecular electronic structure and hence bonding in small metal aggregates and their ions. In addition the group has been concerned with the oxidative processes which these aggregates undergo. In studying gas phase cluster oxidation we are afforded the opportunity to characterize the intermediate region bordered on the one side by the gas phase oxidation of metallic atoms and dimers and on the other by the surface oxidation of the metallic phase. These studies show the promise of providing detailed information on the local micromolecular environment which

characterizes the oxidation of metals and hence the materials degradation associated with such processes.

In order to study small metal clusters, the high temperature laboratory makes use of a number of state-of-the-art technologies taking advantage of sophisticated techniques for the sampling of high temperature, high pressure systems and recent and rapid developments in laser technology. Of primary importance is the development of metal cluster sources which allow not only for the production of the requisite clusters but also provide for their formation at low temperatures ($T \lesssim 300K$). Clusters must be formed at low temperature since the analysis of features which map energy levels, structure, and dynamic behavior may be prohibitive if not impossible at the elevated temperatures required to produce these species through breakdown of the bulk metal. Our experimental methods have focused in large part on a careful mesh of the approproate material science and the techniques of rarefied gas dynamics to produce a "free jet" of cold metal clusters. Once produced, this jet stream of metal clusters is simultaneously probed using a combination of laser fluorescence and mass spectroscopy. A laser intersects the stream of clusters causing their excitation through absorption of particles of light or laser photons. The excited clusters may then emit light characteristic of their structure and dynamic behavior and the spectrum resulting from this emission (fluorescence) of light particles or photons is monitored. In coincidence, the distribution of clusters produced in the jet as a function of various source conditions is monitored by a mass spectrometer.

There are three approaches which we have employed to produce the desired small metal clusters. We have developed techniques to expand both the pure metal vapor $(M_x, M=Na, K, Cu_x, Sb_x)$[1-6] and the metal vapor seeded in a carrier gas flow (helium, argon, N_2, CO)[6]. These approaches provide a <u>continuous</u> source of

small metal clusters which we have probed with continuous wave dye lasers. We have also been involved with the use and development of pulsed cluster sources to produce and study small copper[7] and antimony clusters.[8] Here, we have made use of pulsed laser vaporization (Nd-YAG laser primarily although some attempts were also made with CO_2) where a burst of laser radiation is focused on a metal surface causing intense local heating for a short time frame and creating a gas phase metal plasma. This plasma has been entrained in liquid nitrogen cooled argon or helium and brought to an excitation zone where the molecules in the cold stream are probed with a nitrogen pumped "pulsed" dye laser. Typical molecular internal temperatures are in the range 80-200K.[8] No supersonic expansion is used here and cooling is accomplished through intimate collisional contact with a cold carrier gas.

Our research effort has focused in large part on the alkali (Na_x,K_x...) and coinage metals (Cu_x,Ag_x,...) primarily because of the relative ease with which these studies can be correlated with theory and the expectation that clusters of the Group IA and IB elements will represent the simplest prototypes on which to formulate methods for analyzing the features and behavior of those clusters which will be of future interest. We have been primarily concerned with the study of bound-bound transitions in copper trimer[6] and the characterization of bound-free transitions in sodium trimer.[1-5] Our research thrusts have included

(1) The first studies of metal cluster photodissociation where the absorption of a laser photon leads to the rupture of a polyatomic metal cluster bond. In order to study this process, specifically for the sodium trimer molecule[1-5] we developed the technique of "laser induced atomic fluorescence" (LIAF) where the metal cluster M_n is dissociated with a cw dye laser to yield the fragments M_{n-1} and an electronically excited metal atom, M*. By monitoring

the emission from this electronically excited M*, we have been able to elucidate many features of the bonding and energy levels of sodium trimer, determine an upper bound for the Na_2-Na metal cluster bond energy, and assess the behavior of this cluster under a variety of perturbing conditions. In creating a perturbing condition, we wish to enhance "hot band" fluorescence and the population of levels close to the ground state dissociation limit of a weakly bound metal cluster using the controlled "poisoning" of supersonic expansions which normally produce molecules in the lowest quantum levels of the ground electronic state. These efforts have been quite successful.

In concert with recent studies carried out in the laboratory of Professor Ernst Schumacher,[9] the work in our laboratory provides the first mapping of the electronic states of a polyatomic metal cluster.

Of course, the dissociation of metal clusters is thought to play a role in their catalytic behavior and hence these studies may represent a contribution to our understanding of photocatalytic processes. The LIAF technique is now being extended to processes producing ground state metal atom fragments. In the long term, it is hoped that the technique can be extended to the study of bound-free transitions in copper and silver trimer.

We have constructed a simple and versatile high temperature source which has now been used to obtain the first continuous wave "free-jet" expansion and laser fluorescence spectrum of copper trimer.[6] This system is now under study. Using this source, the extension of our studies to other transition metal elements appears possible and will be a definite future consideration. One possibility includes the extension of the LIAF technique to the study of a strongly photodissociating iron dimer while another might include the study of nickel dimer and trimer.

In order to study cluster oxidation,[10] a stream of metal clusters is made to intersect a tenuous atmosphere of a given oxidant (beam-gas configuration). For sufficiently exoergic processes, the excess energy of reaction may be channeled into electronic excitation of the products of the oxidation process which can then be monitored as chemiluminescing species. In addition, the system is probed through mass spectrometric sampling of the oxidation region, the presence of ions is determined using deflection techniques, and future potential regions for the laser excitation of ground state products are examined using electron impact excitation to form emitting excited electronic states.

The first polyatomic metal cluster oxidation studies have been carried out in our laboratory.[10] Here a beam of sodium clusters (Na_n, $n > 3$) has been reacted with halogen atoms and the chemiluminescent emission corresponding to the process

$$Na_n + X(Cl,Br,I) \rightarrow Na^*_{n-1} + NaX$$

is under study, This system represents a prototype for further metal cluster oxidation studies. In a closely related effort we have applied the techniques of cluster oxidation to obtain the first electronic emission spectrum for the KOH molecule[11] and determine a lower bound for the K-OH bond energy. Because the KOH molecule is one of the most important species present in virtually all energy generating systems, its parameterization represents an important contribution to the development of our ability to control the behavior of the corrosive characteristic of these systems.

The experimental aspects of the research effort are strongly supplemented with quantum chemical calculations on the molecular electronic structure of

metal clusters and their ions.[12-19] These theoretical approaches have provided information on structural trends and the convergence of the properties of small clusters to those of the bulk metal and have now been used by other researchers as an aid to the interpretation of metal cluster spectra for the alkali and coinage metals.

Although alkali cluster ions are expected to play a significant role in a number of important technological processes (e.g. lamps, fusion reactors), little is known about the structure of such ions. As part of a program to stimulate experimental study, we have been among the first to examine the molecular electronic structure of several simple closed shell alkali ions.[12,14,15,19] This work also has as its impetus the belief that metal cluster oxidation environments may be characterized by cluster ion production in secondary collisional processes. Therefore a strong need for cluster parameterization exists.

1. "The Characterization of Supersonic Sodium Vapor Expansions Including Laser Induced Atomic Fluorescence from Trimeric Sodium", with S. A. Pace, D. R. Preuss and G. J. Green, J. Chem. Phys. 76, 2247 (1982).

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7. "Laser Spectroscopy of Cooled Metal Clusters: Copper Dimer", with V. Bondybey and J. H.. English, J. Phys. Chem. 86, 2560 (1982).

8. "Antimony Spectroscopy - Laser Fluorescence Studies of Sb_2-Spectroscopy, Radiative Lifetimes, and the Tentative Identification of the Sb_4 Emission Spectrum", with G. J. Green, S. A. Pace, and V. Bondybey, work in progress.

9. A. Hermann, M. Hofmann, S. Leutewyler, E. Schumacher, and L. Woste, Chem. Phys. Lett. 62, 216 (1979).

10. "Metal Cluster Oxidation: Chemiluminescence from the Reaction of Sodium Polymers (Na_n, $n > 3$) with Halogen Atoms (X=Cl,Br,I)", with W. H. Crumley and D. A. Dixon, J. Chem. Phys. 76, 6439 (1982).

11. "Observation of the KOH Emission Spectrum - A New Lower Bound to the KOH Dissociation Energy", work in progress.

12. "The Electronic Structure of the Lithium Trimer Anion and Cation", J. L. Gole, R. A. Eades, D. A. Dixon and R. Childs, J. Chem. Phys. 72, 6368 (1980).

13. "Theoretical Prediction of the Vibrational Spectra of Group IB Trimers", S. Richtsmeier, J. L. Gole, and D. A. Dixon, Proceedings of Nat. Acad. Sci. 77, 5611 (1980), 78, 7259 (1981).

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15. "The Electronic Structure of Alkali Trimer Anions and Cations", with R. A. Eades M. L. Hendewerk, R. Frey and D. A. Dixon, J. Chem. Phys. 76, 3075 (1982).

16. "The Structure of Mixed Alkali Metal Trimers", with S. C. Richtsmeier, M. L. Hendewerk and D. A. Dixon, J. Phys. Chem. 86, 3932 (1982).

17. "The Structure of Group IB Metal Clusters, M_n, n = 4-6", with S. C. Richtsmeier and D. A. Dixon, J. Phys. Chem. 86, 3937 (1982).

18. "The Structure of Group IA Metal Clusters, M_n, n = 4-6", with S. C. Richtsmeier and D. A. Dixon, J. Phys. Chem. 86, 3942 (1982).

19. "Electron Affinities of the Alkali Dimers Na_2, K_2, and Rb_2", with H. Partridge, D. A. Dixon, S. P. Walch, and C. W. Bauschlicher, J. Chem.